Molybdenum-based polyoxometalates as highly active and selective catalysts for the epimerization of aldoses

Supporting information

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Table S1. The effect of pH on the epimerization of glucose using $H_3PMo_{12}O_{40}$ as catalyst[a]

Entry	PH	Time (min)	Temperature (^oC)	Glucose conversion (%)	Mannose Selectivity (%)
1	1.14	60	80	26.2±1.1	91
2	1.69	60	80	25.6±0.6	90
3	2.37	60	80	25.5±0.9	93
4	3.78	60	80	26.1±0.8	91
5	4.12	60	80	25.4±0.8	94
6	4.86	60	80	22.6±0.7	92
7	5.02	60	80	16.7±0.3	94
8	5.13	60	80	14.7±0.5	95

[a]Reaction condition: For all the reactions, the molar ratio of Mo to glucose was kept constant at 1:50 for all the runs. pH of the solutions was adjusted using concentrated HCl or NH_4OH.

Table S2. The effect of pH on the epimerization of glucose using $Ag_{3.03}PMo_{12}O_{40}$ as catalyst[a]

Entry	PH	Time (min)	Temperature (^oC)	Glucose conversion (%)	Mannose Selectivity (%)
1	1.22	60	80	25.1±0.8	92
2	1.60	60	80	24.8±0.6	91
3	2.41	60	80	25.3±0.9	90
4	3.68	60	80	26.0±0.8	92
5	4.06	60	80	24.5±0.6	95
6	4.90	60	80	21.7±0.5	93
7	5.01	60	80	15.3±0.5	94
8	5.22	60	80	12.6±0.4	93

[a]Reaction conditions: For all the reactions, the molar ratio of Mo to glucose was kept constant at 1:50 for all the runs. pH of the solutions was adjusted using concentrated HCl or NH_4OH.

Table S3. The effect of pH on the epimerization of glucose using $Sn_{0.76}PMo_{12}O_{40}$ as catalyst[a]

Entry	PH	Time (min)	Temperature (^{o}C)	Glucose conversion (%)	Mannose Selectivity (%)
1	1.18	60	80	25.4±1.0	90
2	1.56	60	80	25.0±1.1	91
3	2.38	60	80	25.7±0.8	94
4	3.75	60	80	25.2±0.7	93
5	4.10	60	80	24.7±0.5	91
6	4.88	60	80	20.8±0.7	92
7	4.97	60	80	14.4±0.4	92
8	5.06	60	80	12.3±0.6	94

[a]Reaction condition: For all the reactions, the molar ratio of Mo to glucose was kept constant at 1:50 for all the runs. pH of the solutions was adjusted using concentrated HCl or NH_4OH.

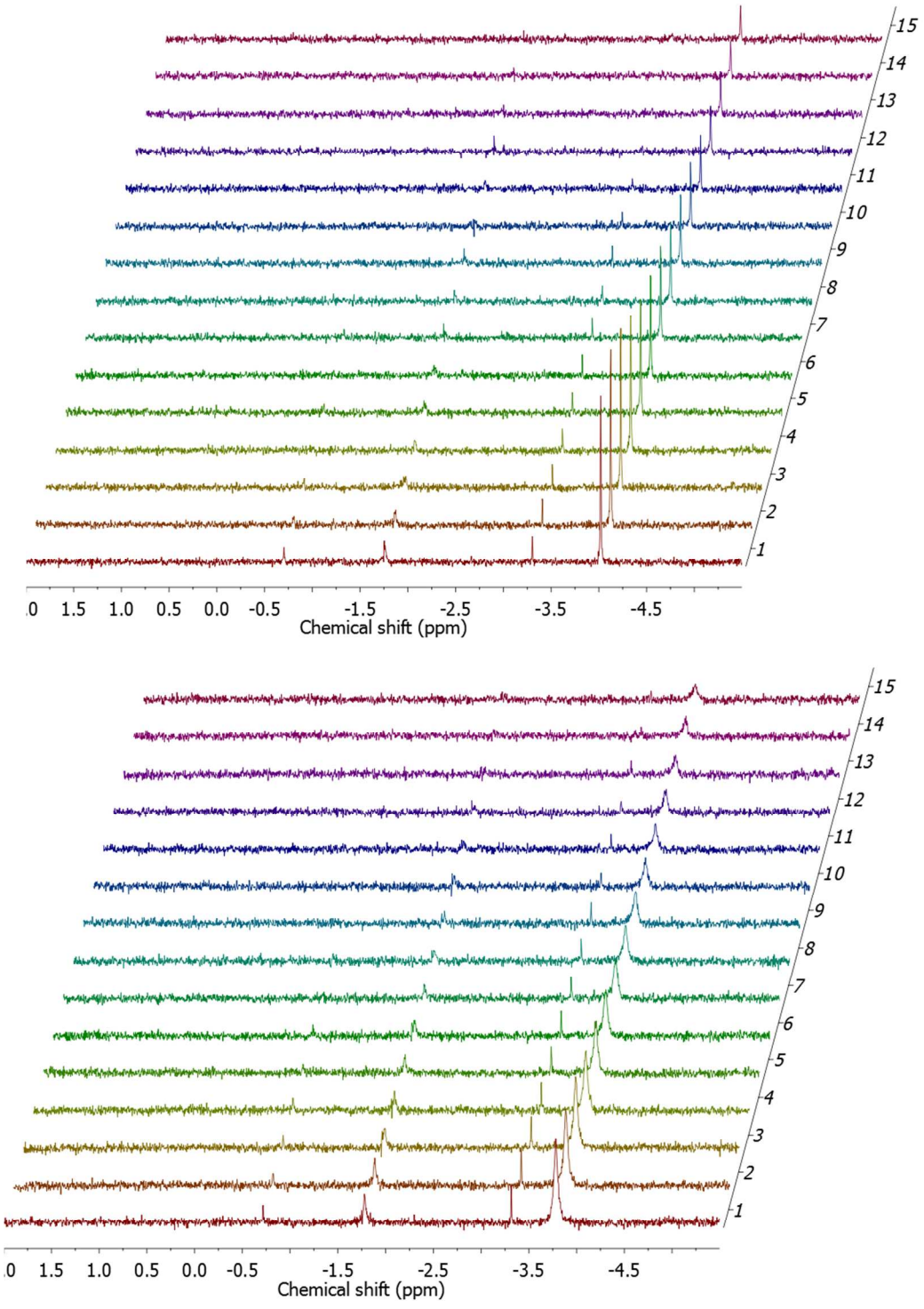

Figure S1. ^{31}P DOSY NMR spectra of 0.1 M of $H_3PMo_{12}O_{40}$ aqueous solution with glucose (a) before and (b) after reaction

Table S4. Chemical shift and width of different species in $H_3PMo_{12}O_{40}$ solution without glucose

Species	Chemical shift (ppm)		Width (ppm)	
	Before reaction	After reaction	Before reaction	After reaction
1	-0.70	-0.70	3.80	3.50
2	-1.78	-1.78	7.74	8.15
3	-3.29	-3.29	2.91	2.17
4	-4.01	-4.01	2.26	2.30

Table S5. Chemical shift and width of different species in $H_3PMo_{12}O_{40}$ solution with glucose

Species	Chemical shift (ppm)		Width (ppm)	
	Before reaction	After reaction	Before reaction	After reaction
1	-0.74	-0.74	3.92	3.74
2	-1.80	-1.80	7.52	6.63
3	-3.34	-3.34	2.18	2.36
4	-4.03	-3.92	3.02	5.70

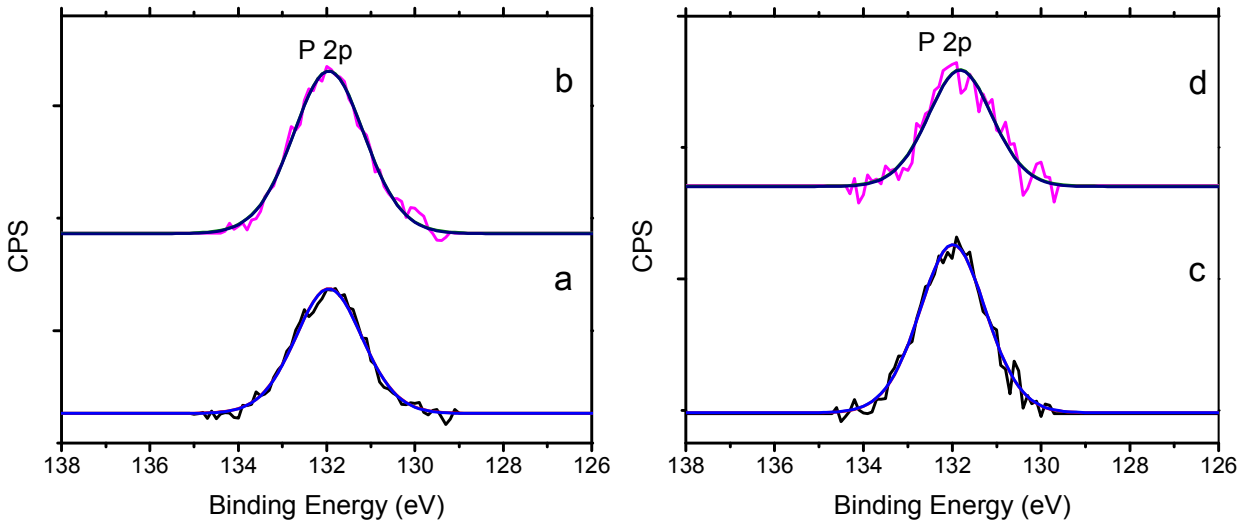

Figure S2. XPS spectra of P in $Ag_3PMo_{12}O_{40}$ precipitated by $AgNO_3$ from $H_3PMo_{12}O_{40}$ solution without glucose (a) before and (b) after reaction; with glucose (c) before and (d) after reaction. (No P oxidation state change was detected.)

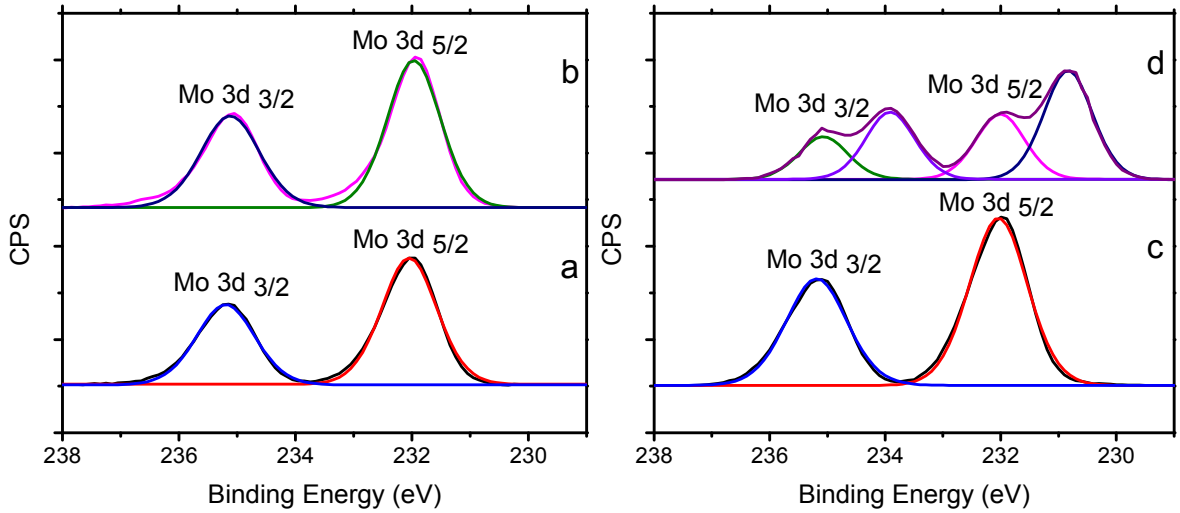

Figure S3. XPS spectra of Mo in $Sn_{0.75}PMo_{12}O_{40}$ precipitated by $SnCl_4$ from $H_3PMo_{12}O_{40}$ solution without glucose (a) before and (b) after reaction; with glucose (c) before and (d) after reaction.

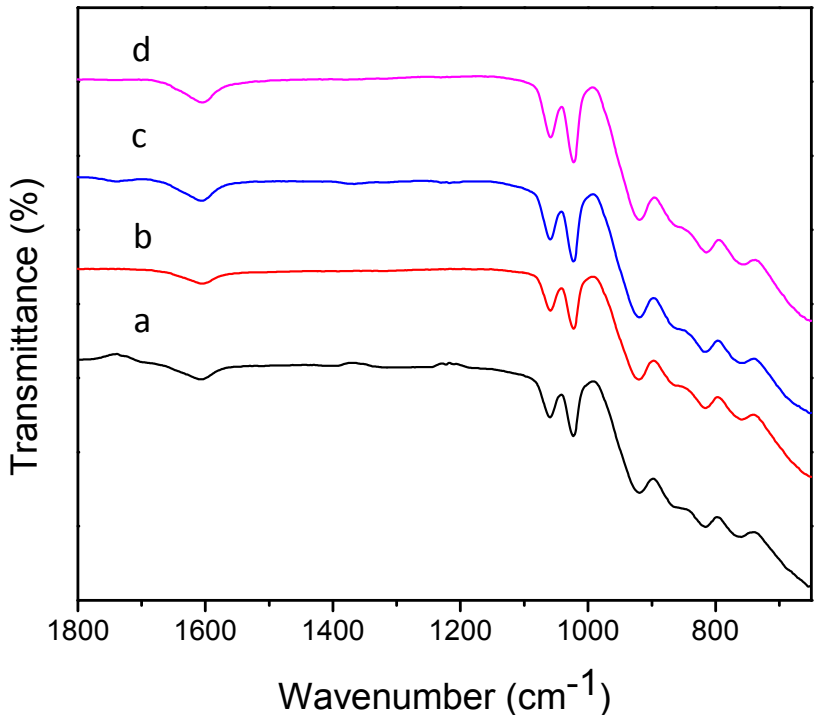

Figure S4. FTIR spectra of $Ag_3PMo_{12}O_{40}$ obtained from precipitating $PMo_{12}O_{40}^{3-}$ from solution using $AgNO_3$ (a) before and (b) after heating at 80°C for 60 min in the absence of glucose; (c) before and (d) after reaction with glucose at 80°C for 60 min.

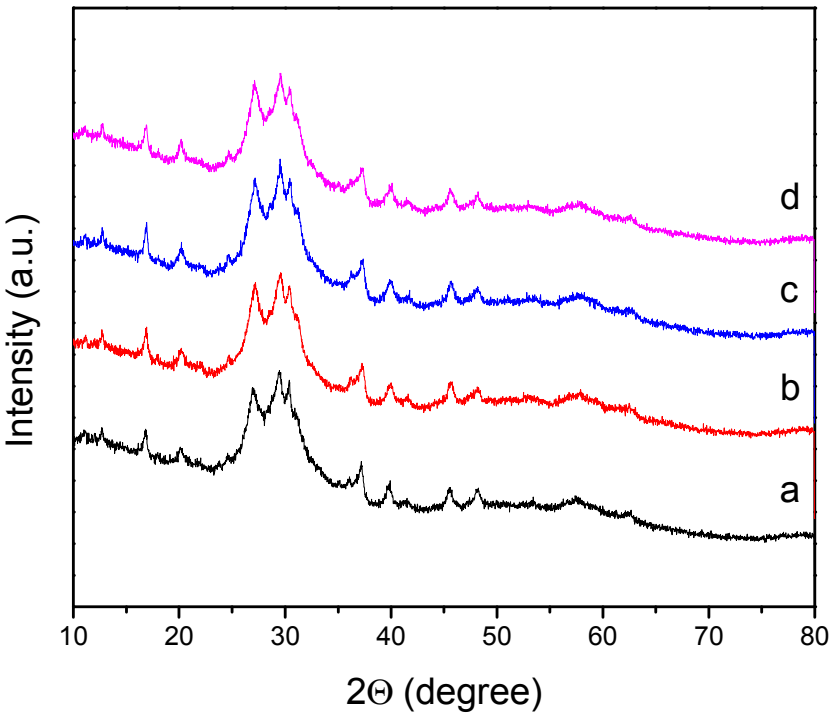

Figure S5. XRD patterns of $Ag_3PMo_{12}O_{40}$ obtained from precipitating $PMo_{12}O_{40}^{3-}$ from solution using $AgNO_3$ (a) before and (b) after heating at 80°C for 60 minutes in the absence of glucose; (c) before and (d) after reaction with glucose at 80°C for 60 minutes.

S.3. ^{13}C kinetic isotope effect calculation based on experimental data

Figure 8 shows the fits of the experimental data to kinetic models assuming the reversible glucose epimerization is a first-order reaction. The formation of mannose follows the equation:

$$C_m(t) = C_{m,e}\left(1 - e^{-\frac{t}{\tau}}\right)$$

Where $C_m(t)$ and $C_{m,e}$ are the concentrations of mannose at time t and equilibrium, respectively, and$\tau$is the time constant for the approach to equilibrium.

Initial turnover rates for unlabeled and labeled glucose were calculated from extrapolation to zero time and non-zero values for rates of formation of mannose.

The ^{13}C kinetic isotope effect can be calculated as follows:

$$\frac{k(glucose)}{k(13C-glucose)} = \frac{r(glucose)/C(glucose)}{r(13C-glucose)/C(13C-glucose)}$$ where k is the rate constant, r represents reaction rate and C is concentration.

At t = 0 min, $C(glucose) = C(13C - glucose)$

so $\frac{k(glucose)}{k(13C-glucose)} = \frac{r(glucose)}{r(13C-glucose)} = \frac{Slope(glucose)}{Slope(13C-glucose)} = 1.06 \pm 0.03$.

S.4. ^{13}C kinetic isotope effect via theoretical estimation:

The theoretical kinetic isotope effect is estimated via the equation derived from transition state theory.

$$\frac{k\ (12C-12C)}{k\ (13C-12C)} = \exp\left(\frac{ZPE\ (12C-12C) - ZPE\ (13C-12C)}{kT}\right) \qquad \text{Eq S1}$$

where $ZPE = \frac{1}{2}\ h\ c\ \nu$, h is the Planck's constant (6.63*10^{-34} m^{2}kg/s), c is the speed of light (2.998*10^8 m/s), ν is the vibrational frequency of a C-C bond stretching, k is the Boltzman constant (1.38*10^{-23} m^{2}kg/s^2/K) and T is the temperature (353 K).

Substitute ZPE with $\frac{1}{2}\ h\ c\ \nu$, so Eq S1 can be re-written as

$$\frac{k\ (12C-12C)}{k\ (13C-12C)} = \exp\left(\frac{\frac{1}{2}h\ c\ (\nu\ (12C-12C) - \nu\ (13C-12C))}{kT}\right)$$

The stretching vibration between C1 and C2 in unlabeled and 13C labeled glucose is 1147 and 1136 cm^{-1}, respectively, based on the FTIR spectra (Figure S6), which has a good agreement

with literature reports.[1-3] So in the equation shown above, $\nu\ (12C - 12C) = 1147\ cm^{-1}$, $\nu\ (13C - 12C) = 1136\ cm^{-1}$, and the formation of the C1-C3 bond in mannose is also assumed to proceed via a stretching vibration.

Based on these assumptions, the kinetic isotope effect (KIE), the ratio between the rate constant for epimerization of unlabeled glucose (containing ^{12}C1-^{12}C2 bond) and the one for epimerization of labeled (^{13}C-1)glucose (containing ^{13}C1-^{12}C2 bond) is $\frac{k\ (12C-12C)}{k\ (13C-12C)} = 1.023$

The theoretical KIE is in good agreement with our experimental results shown above.

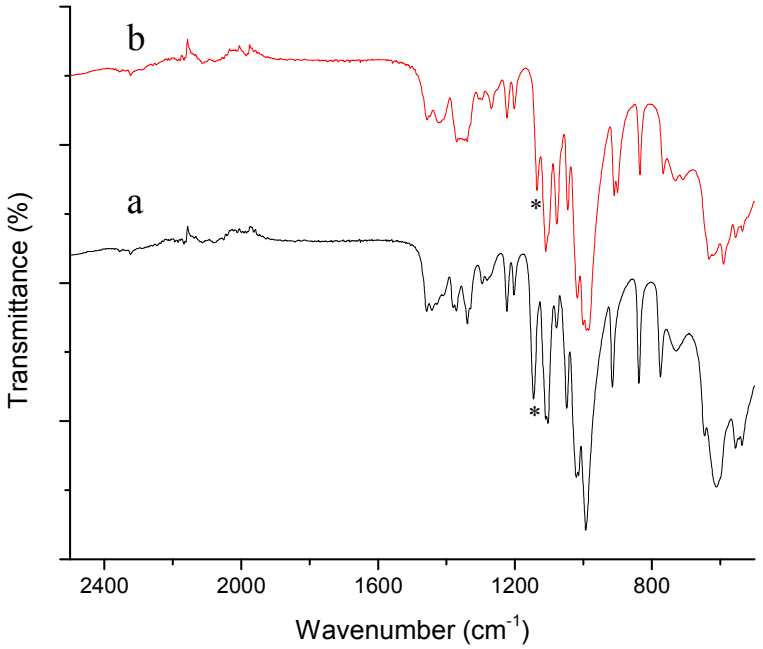

Figure S6. FTIR spectra of (a) unlabeled glucose and (b) ^{13}C labeled (C1) glucose.

References

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(2) Ibrahim, M.; Alaam, M.; El-Haes, H.; Jalbout, A. F.; Leon, A. d. *Eclética Quím.* **2006**, 31, 15-21.
(3) Urano, T.; Hamaguchi, H. o.; Tasumi, M.; Yamanouchi, K.; Tsuchiya, S.; Gustafson, T. L. *J. Chem. Phys.* **1989**, 91, 3884-3894.